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KINETIC-ENERGY DISTRIBUTIONS OF IONS SAMPLED FROM RADIO-FREQUENCY DISCHARGES IN HELIUM, NITROGEN, AND OXYGEN

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ABSTRACT

Mass-resolved ion kinetic energy distributions are measured for radio-frequency (rf) discharges sustained in helium, nitrogen, and oxygen in a parallel-plate plasma reactor. The dominant ions for each of the gases are observed to be the parent ions He^+ , N_2^+ , and O_2^+ , respectively, over a wide range of pressures (1.3 to 67 Pa) with an applied rf voltage of 200 V. Ion kinetic-energy distributions at the grounded electrode were measured for these ions, as well as for less abundant ions, such as He_2^+ , N^+ , N_2H^+ , N_3^+ , N_4^+ , O^+ , and O_3^+ .

INTRODUCTION

As greater demands by the semiconductor industry are placed on radio-frequency plasma etching processes, improved control and characterization of the etching plasma becomes essential. The development of diagnostics to probe the microscopic properties of the rf discharge may provide the means to generate the repeatable, well-characterized plasmas required for future etching processes. One diagnostic which shows promise as an applied sensor is mass spectrometry with ion energy analysis, since ion bombardment of surfaces plays a significant role in the etching of semiconductor materials [1].

In this paper we present mass-resolved measurements of the kinetic energies of ions produced in rf discharges sustained in helium, nitrogen, and oxygen. These three gases were chosen to allow the evaluation of the diagnostic technique under well-controlled but widely varying plasma conditions, because they are commonly used in theoretical models of rf plasmas, and to investigate the basic physical and chemical processes that occur within the discharges. Analysis of the identities, relative signal intensities, and shapes of the kinetic-energy distributions of the ions as a function of pressure provided information about the formation and transport of ions within the plasma.

EXPERIMENT

Ions were sampled through a 0.1 mm hole in the stainless-steel [2], grounded electrode of a Gaseous Electronics Conference rf Reference Cell [3] with 10 cm diameter parallel-plate electrodes spaced 2.5 cm apart. The ions are mass and energy analyzed by a quadrupole mass spectrometer coupled to an electrostatic ion-energy analyzer [4]. To obtain an ion kinetic-energy distribution (IED), the mass spectrometer is set to a particular mass-to-charge ratio, and the energy of the ions entering the energy analyzer is scanned. The full width-at-half maximum energy resolution of the energy analyzer is approximately 1.5 eV. The same instrumental settings of the mass spectrometer-energy analyzer were used for all IEDs obtained with a specific gas, so as to allow a comparison of the relative intensities of the different ions at each pressure.

For all of the IEDs presented here the peak-to-peak applied rf voltage (V_{pp}) was held constant at 200 V, the gas flow was 1.7×10^{-2} Pa m³/s (10 sccm), and the pressures were varied between 1.3 and 67 Pa, depending upon the gas. Gas is supplied through a showerhead arrangement of holes in the aluminum, capacitively-coupled, powered electrode. The voltage and current waveforms are measured at the powered electrode, and analyzed using an equivalent circuit model of the GEC Cell [3,5].

RESULTS AND DISCUSSION

Helium

Measured IEDs for the dominant ions, He^+ and He_2^+ , observed in helium plasmas with gas pressures varying from 8.0 to 66.7 Pa (60 to 500 mTorr) are shown in Fig. 1. The flux of He^+ striking the grounded electrode far exceeds that of He_2^+ for all conditions presented here. This agrees with the assumption generally made when modeling helium discharges, that He^+ is the dominant ion [6]. The shapes of the IEDs for He^+ are determined primarily by symmetric charge-exchange collisions experienced by

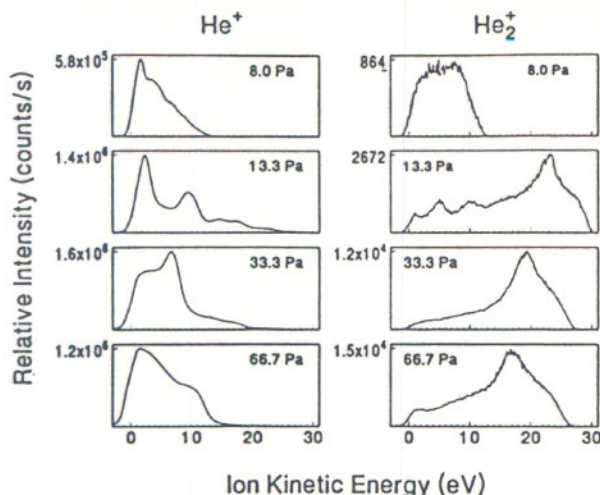


Fig. 1 Ion kinetic-energy distributions sampled from rf discharges sustained in helium for various pressures.

ions as they traverse the sheath from the glow region of the discharge to the electrode surface. These collisions shift the mean energy of the distributions toward lower energies, and produce secondary peaks, or maxima, similar to those observed for Ar^+ ions sampled from argon plasmas [4,7]. The reduction of mean ion energies is observed to increase as the gas pressure, and thus the probability of collisions, increases.

He_2^+ ions are formed primarily by three-body collisions [8] or collisions between ground state and highly-excited neutrals [9] within the bulk of the discharge, and are observed to increase significantly in intensity with increasing gas pressure. Because charge-exchange collisions do not effect He_2^+ transport across the sheath, the He_2^+ IEDs remain peaked at the highest energies determined by the plasma potential, even as the pressure increases to 66.7 Pa.

Dramatic changes are observed in the shapes of the IEDs for both He^+ and He_2^+ as the pressure is increased from 8.0 to 13.3 Pa. These changes correlate with changes in the optical emission, where the discharge is observed to shift from a dim, diffuse glow to a brighter, confined mode, and changes in the voltage waveforms, where the self-bias voltage changes from -50 to -74 V.

The measurements of Flender and Wiesemann [10] provide the only other experimental data in the literature on IEDs from pure helium rf discharges. However, a quantitative comparison with the present data is not possible because of differences in discharge conditions, and because mass analysis was not used in this earlier work.

Nitrogen

Kinetic-energy distributions of the major ions sampled from nitrogen plasmas with pressures ranging from 4.0 to 33.3 Pa (30 to 250 mTorr) are presented in Fig. 2. The dominant ion is N_2^+ for all pressures, with N^+ being the second most intense ion at low pressures. For pressures exceeding 9.3 Pa, the "impurity" ion N_2H^+ is observed to become the ion with the second largest intensity. N_2H^+ is formed by the fast reaction of N_2^+ ions with residual water molecules in the plasma gas [11]. It is significant that this ion can account for a substantial fraction of the ion flux, even in a "clean" reactor, such as used here, which has a base pressure of 10^{-5} Pa and uses 99.999% pure gases. The IEDs for the N_3^+ and N_4^+ (not shown) exhibit shapes similar to those of N^+ , but with intensities that are, respectively, about 10 and 200 times lower.

The shapes of the IEDs for N_2^+ are determined primarily by charge-transfer collisions in the sheath as is evident by the secondary maxima observed in the measured IEDs, and by the downward shift in mean energies with increasing pressure. The IEDs for N_2H^+ exhibit similar shapes and structure which suggest that they can be formed both in the bulk and in the sheath by ion-molecule reactions. IEDs for N^+ are peaked between 20 and 30 eV for pressures of 13.3 Pa and below, since N^+ does not experience significant loss of energy due to collisions in the sheath. This allows these ions to gain kinetic energies corresponding to the time-averaged voltage drop across the ground sheath, and therefore can be used to monitor the plasma potential of the discharge. The increase in maximum ion energy observed for N^+ correlates with changes in the self-bias voltage.

Oxygen

Kinetic-energy distributions of O^+ , O_2^+ , and O_3^+ sampled from an oxygen discharge are presented in Fig. 3 for pressures ranging from 1.3 to 33.3 Pa (10 to 250 mTorr). At 1.3 Pa, the intensity of O_2^+ exceeds that of O^+ by approximately a factor of ten, in agreement with previous measurements [12,13]. The intensity of O_3^+ is nearly three orders of magnitude below O_2^+ at 1.3 Pa. At higher pressures, the intensity of O^+ and O_3^+ drop significantly, and the O_2^+ intensity exceeds all other ion intensities by more than a factor of 1000. The drop in O^+ intensity with increasing pressure is possibly due to the increased role of asymmetric charge-transfer collisions that convert O^+ to O_2^+ .

At low pressures, all three ions exhibit peaks near 20 eV that are indicative of relatively collisionless transport across the sheath. The double-peak structure that is most evident for O^+ is the previously observed "saddle structure" [13] that is the result of rf modulation of the ion energies in collisionless sheaths. As the

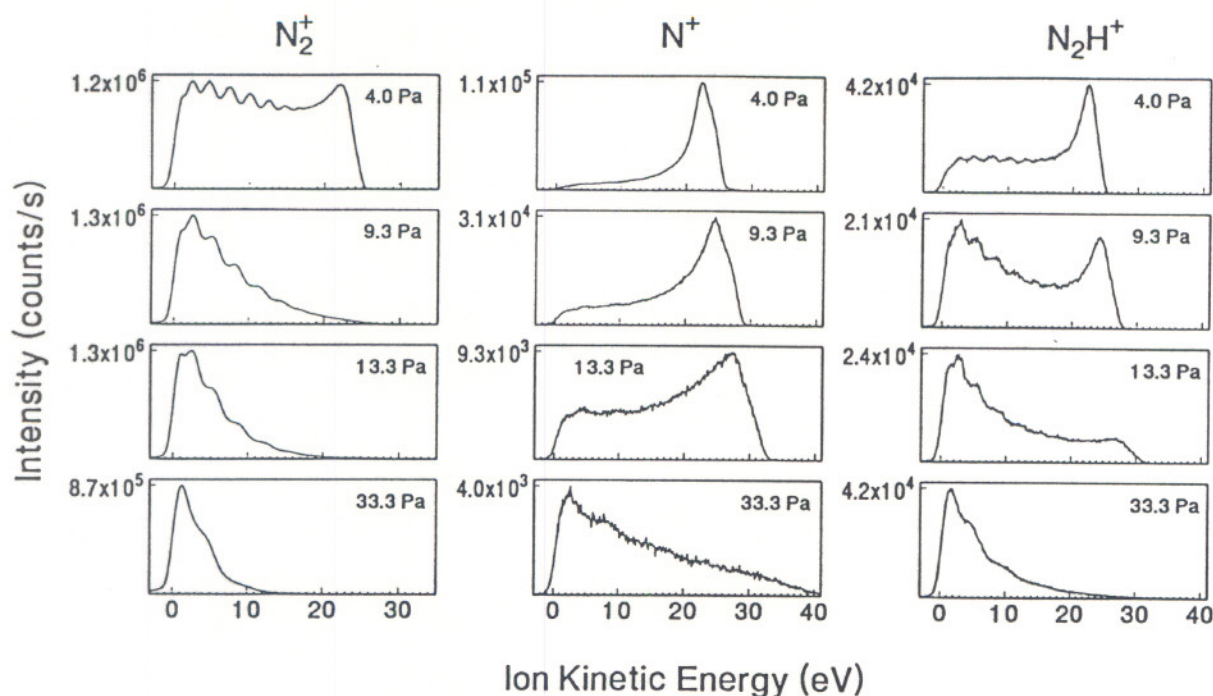


Fig. 2. Ion kinetic-energy distributions sampled from rf discharges sustained in nitrogen for various pressures.

pressure increases, the O_2^+ IEDs exhibit a shift toward lower mean energies and an increase in the magnitude of secondary maxima, resulting from increased numbers of charge-exchange collisions in the sheath. The IEDs for O^+ and O_3^+ remain relatively featureless as the pressure increases, indicating that these ions are formed primarily in the bulk region of the plasma, and not in the sheath.

Several studies of the kinetic energies of ions from oxygen plasmas have been presented in the literature [7,10,12-14], but only one [12] study has utilized a combination of mass and energy analysis. While the reactor and diagnostic equipment designs differ significantly in these experiments, the results are all consistent with the IEDs presented here. While only rudimentary modeling [7,15] of IEDs for oxygen plasmas have been performed, the IEDs presented here are in qualitative agreement with the published data. Additionally, the data from the present work are in agreement with many of the assumptions and conclusions made about relative ion densities and energies in modeling other aspects of oxygen discharges [6,16].

CONCLUSIONS

Measurements were made of mass-resolved ion-energy distributions for rf plasmas in helium, nitrogen, and oxygen as a function of gas pressure. The dominant ions detected from these plasmas were He^+ , N_2^+ , and O_2^+ , respectively, and the shape of the

IEDs for these ions were determined primarily by symmetric charge-transfer collisions while being accelerated across the plasma sheath. Other less abundant ions were also detected that are useful in determining the plasma potential of the discharge.

REFERENCES

- [*] Present address: Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, NM
- [1] Coburn, J. W., "Role of ions in reactive ion etching" *J. Vac. Sci. Technol. A* 12, 1417-1424, 1994.
- [2] Ions were sampled through an orifice in an electrode made of stainless in order to minimize the effects of surface charging. See Olthoff, J. K., Van Brunt, R. J., and Radovanov, S. B., "Effect of electrode material on measured ion energy distributions in radio-frequency discharges" *Appl. Phys. Lett.*, in press.
- [3] Hargis, P. J., et al., "The Gaseous Electronics Conference radio-frequency reference cell: A defined parallel-plate radio-frequency system for experimental and theoretical studies of plasma-processing discharges" *Rev. Sci. Instrum.* 65, 140-154, 1994.
- [4] Olthoff, J. K., Van Brunt, R. J., Radovanov, S. B., Rees, J. A., and Surowiec, R., "Kinetic-energy distributions of ions sampled from argon plasmas in a parallel-plate, radio-frequency reference cell" *J. Appl. Phys.* 75, 115-125, 1994.
- [5] Sobolewski, M. A., "Electrical characterization of radio-frequency discharges in the Gaseous Electronics Conference Reference Cell" *J. Vac. Sci. Technol. A* 10, 3550-3562, 1992.

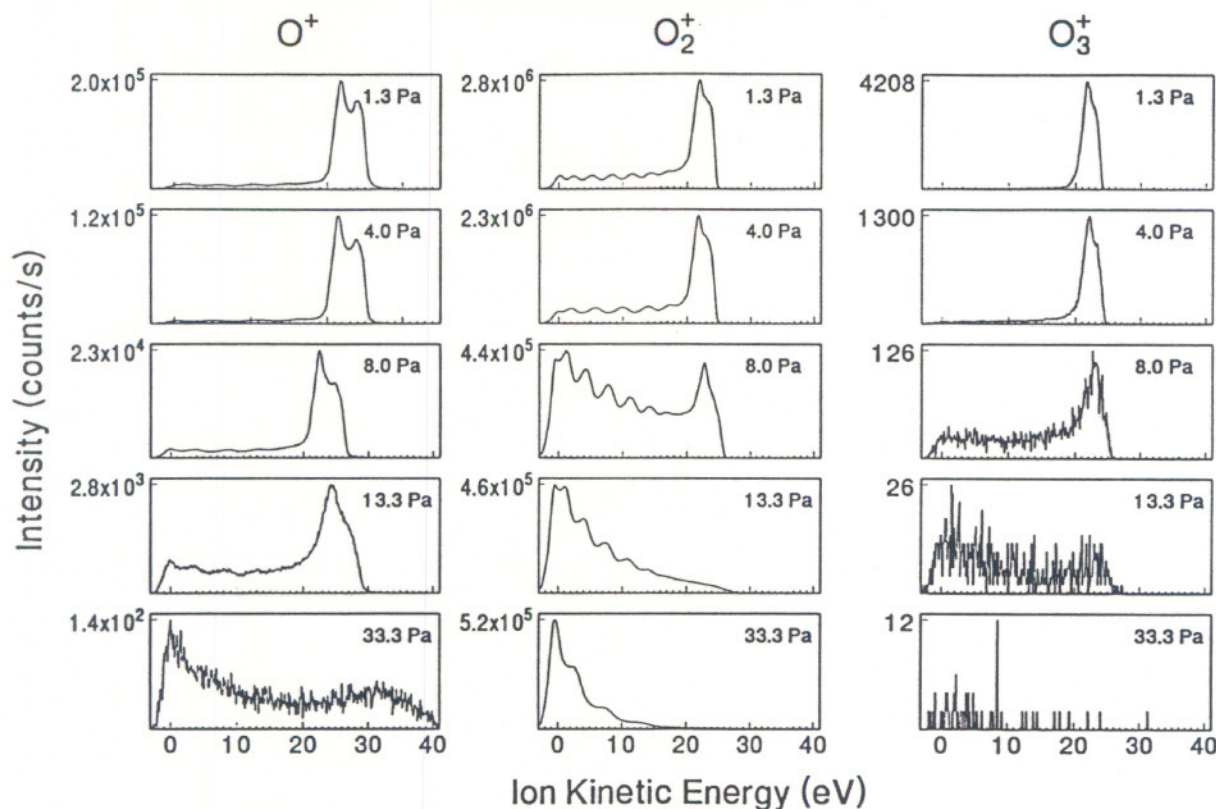


Fig. 3. Ion kinetic-energy distributions sampled from rf discharges sustained in oxygen for various pressures.

[6] Sommerer, T. J. and Kushner, M. J., "Numerical investigation of the kinetics and chemistry of rf glow discharge plasmas sustained in He, N₂, O₂, He/N₂/O₂, He/CF₄/O₂, and SiH₄/NH₃ using a Monte Carlo-fluid hybrid model" *J. Appl. Phys.* **71**, 1654-1673, 1992.

[7] Wild, C. and Koidl, P., "Ion and electron dynamics in the sheath of radio-frequency glow discharges" *J. Appl. Phys.* **69**, 2909-2922, 1991.

[8] Johnsen, R., Chen, A., and Biondi, M. A., "Three-body association reactions of He⁺, Ne⁺, and Ar⁺ ions in their parent gases from 78 to 300 K" *J. Chem. Phys.* **73**, 1717-1720, 1980.

[9] Hornbeck, J. A., and Molnar, J. P., "Mass spectrometric studies of molecular ions in the noble gases" *Phys. Rev.* **84**, 621-625, 1951.

[10] Flender, U., and Wiesemann, K., "Ion distribution functions behind an RF sheath" *J. Phys. D: Appl. Phys.* **27**, 509-521, 1994.

[11] Howorka, F., Lindinger, W. and Varney, R. N., "Reaction rate constants in steady-state hollow cathode discharges: N₂ + H₂O reactions" *J. Chem. Phys.* **61**, 1180-1188, 1974.

[12] Janes, J. and Huth, C., "Energy-resolved angular distributions of O⁺ ions at the radio-frequency-powered electrode in reactive ion etching" *J. Vac. Sci. Technol. A* **10**, 3086-3091, 1992. Janes, J. and Huth, C., "Bombardment energies of O₂⁺ in low pressure reactive ion etching" *Appl. Phys. Lett.* **61**, 261-263, 1992.

[13] Kuypers, A. D., and Hopman, H. J., "Ion energy measurement at the powered electrode in an rf discharge" *J. Appl. Phys.* **63**, 1894-1898, 1988.

[14] Manenschijn, A., Janssen, G. C. A. M., van der Drift, E. and Radelaar, S., "Measurement of ion impact energy and ion flux at the rf electrode of a parallel plate reactive ion etcher" *J. Appl. Phys.* **69**, 1253-1262, 1991.

[15] Field, D., Klemperer, D. F., May, P. W. and Song, Y. P., "Ion energy distributions in radio-frequency discharges" *J. Appl. Phys.* **70**, 82-92, 1991.

[16] Shibata, M., Nakano, N. and Makabe, T., "O₂ rf discharge structure in parallel plates reactor at 13.56 MHz for material processing" *J. Appl. Phys.*, submitted.